

THE ABSORPTION AND REFRACTION OF
CENTIMETER MICROWAVES BY WATER

A THESIS

Presented to
the Faculty of the Division of Graduate Studies
Georgia Institute of Technology

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Physics

by

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June, 1950

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CENTIMETER MICROWAVES BY WATER

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June 1, 1950

TABLE OF CONTENTS

	PAGE
Summary.....	1
Introduction.....	3
Theoretical Basis for Calculations.....	4
Experimental Procedure.....	6
Theoretical and Experimental Values.....	14
Discussion of Results.....	20
Dielectric Theory in the Regions of Dipolar Dispersion.....	21
Theory of Debye.....	24
Theory of Onsager.....	26
REFERENCES.....	31
APPENDIX.....	33

LIST OF TABLES

TABLE NO.		PAGE
I.	Static and High Frequency Dielectric Constants and Relaxation Time of Water as Given by Saxton.....	15
II.	Theoretical and Experimental Values of \underline{n} and \underline{k}	16

LIST OF FIGURES

FIGURE NO.		
1.	Simplified Schematic of Laboratory Arrangement for Measuring Attenuation and Phase Shift through Water Sample.....	8
2.	Water Sample Holder for Transmission Measurements of Attenuation and Phase Shift in Wave Guide.....	8
3.	Sample Holder for Measurement of Attenuation and Phase Shift of Centimeter Microwaves by Water.....	12
4.	Laboratory Arrangement for Measurement of Attenuation and Phase Shift of Centimeter Microwaves by Water....	13
5.	The Absorption Coefficient and Index of Refraction of Water versus Temperature at 1.25 cm.....	17
6.	Theoretical Curves Showing Variation of Absorption Coefficient, \underline{k} , and Refractive Index, \underline{n} , with Wave Length (Temperature = 20°C).....	19

THE ABSORPTION AND REFRACTION OF CENTIMETER MICROWAVES BY WATER

SUMMARY

Heretofore the index of refraction of a high loss liquid for electromagnetic waves has been found by first measuring the reflection coefficient. This paper describes a method by which both the index of refraction and the absorption coefficient are determined by measuring the phase shift and attenuation by a thin layer of the liquid. Two transmission methods are described, both giving essentially the same results. In the first arrangement the sample of water was placed in the wave guide while in the second two electromagnetic horns were placed face to face and immersed in the liquid.

Measurements were made between 0 and 50 degrees centigrade at 1.15, 1.25, and 1.35 centimeters with ordinary tap water. Measurements were made on distilled water and various concentrations of salt water at 1.25 centimeters and 20 degrees centigrade. No measurable difference could be found between tap, distilled, and salt water. The results compare favorably with the semitheoretical results of Saxton and Lane, and the experimental results of Collie, Ritson and Hasted.

The theoretical expression for the dielectric constant of a polar liquid or gas in the region of anomalous dispersion is derived using the molecular distribution function of Debye and a simple expression for the field on a molecular dipole. The same expression

is derived from the field equations of Clausius-Mosotti and Onsager. Values calculated from this expression are compared with experimental results.

INTRODUCTION

Much is known about the absorption and refraction of dielectrics in the infra-red, visible, and shorter wave length regions where the absorbed energy is used primarily to induce atomic and electronic vibrations. Little is known, however, about dielectric properties at much longer wave lengths where the absorbed energy tends to induce molecular rotation. The present theories of dispersion are quite adequate for many gases and vapors, and also for a large number of polar molecules in solution. With pure liquids, on the other hand, new influences come into play, and the absorption at microwave frequencies consists of a much broader region than the absorption band of a gas or vapor. The values of the absorption coefficient and index of refraction also change much more rapidly with a change in the temperature of the dielectric. Drude first noticed this "anomalous dispersion" and Debye¹ formulated a theoretical basis for this phenomenon by the use of the internal field theory of Clausius and Mosotti. Debye also introduced the idea of a "relaxation time" for the process of molecular rotation. Later theories of Frohlich,² Onsager,³ Eyring,⁴ Kirkwood,⁵ Kauzmann,⁶ and others have attempted to overcome the defects of Debye's original theory -- in particular his use of the Clausius-Mosotti internal field or his neglect of the dipole interaction field.

Regardless of the particular theory used, an expression for the dielectric constant of a polar liquid in the region of anomalous dispersion can be derived, and the results differ only in the value of the relaxation time. Since the relaxation time must at present be determined by experimental methods, this matter is of little consequence.

THEORETICAL BASIS FOR CALCULATIONS

In the region of anomalous dispersion where refraction is accompanied by absorption, the relative dielectric constant is expressed as a complex number,

$$\epsilon = \epsilon' - j\epsilon'' , \quad (1)$$

where the imaginary part is associated with the absorption.

According to the formal theory of the propagation of electromagnetic waves, ϵ is equal to the square of the generalized refractive index, but since ϵ is here a complex quantity, the generalized refractive index will also have an imaginary part. In the usual way we therefore put

$$\epsilon = (n - jk)^2 . \quad (2)$$

The meaning of the two components of the dielectric constant is seen if it is remembered that the field intensity of a plane wave traveling in the z direction is proportional to the expression,

$$e^{j\omega \left[t - \frac{(n - jk)}{c} \tilde{z} \right]} = e^{-\frac{\omega k \tilde{z}}{c}} \cdot e^{j\omega \left[t - \frac{n}{c} \tilde{z} \right]} . \quad (3)$$

If the wave length in free space is λ_0 , the wave length in the medium is $\frac{\lambda_0}{n}$ and the amplitude is decreased by the factor $e^{-2k\pi}$ after the wave has traveled a distance of one wave length. The absorption may be expressed in decibels (db) by

$$\text{Number of db} = \frac{40\pi}{2.303} \frac{k\tilde{z}}{\lambda_0} . \quad (4)$$

Similarly the phase change in radians may be expressed as

$$\phi = \frac{2\pi n}{\lambda_0} z. \quad (5)$$

By equating equations (1) and (2) we obtain the expressions for the real and imaginary components of the dielectric constant in terms of the index of refraction and the absorption coefficient:

$$\epsilon' = n^2 - k^2 \quad (6)$$

and

$$\epsilon'' = 2nk. \quad (7)$$

EXPERIMENTAL PROCEDURE

For electromagnetic waves propagated through a dielectric sample restricted by a rectangular wave guide, equations (4) and (5) for an unrestricted medium do not necessarily hold. Energy propagated in the TE_{01} mode travels at an angle θ from the walls of the guide, given by

$$\sin \theta = \frac{\lambda_0}{\lambda_c},$$

where λ_0 is the free space wave length and λ_c is the cutoff wave length equal to twice the larger of the two inside dimensions of the wave guide. The angle through a dielectric section, of refractive index n , in the guide will then be given by

$$\sin \theta = \frac{\lambda_0}{n \lambda_c}.$$

This may be considered as an increase in path distance given by

$$\tilde{z}' = \frac{\tilde{z}}{\cos \left(\sin^{-1} \frac{\lambda_0}{n \lambda_c} \right)}.$$

For a wave length of 1.25 centimeters and for the particular size of wave guide used in this experiment, an index of refraction of four increases the path distance through the sample less than one per cent. Since n is greater than four for water at this wave length, this error may be neglected.

The microwave power source used was a 2K33 klystron oscillator modulated by a 2.5 kc square wave. A 1N26 crystal, tuned amplifier, and vacuum tube amplifier were used to detect the signal. Figure 1 shows the equipment arrangement for the measurement of the attenuation and phase shift.

Since transmission through only extremely thin samples of water is practicable at centimeter wave lengths, direct measurement of the length of water path is difficult. To simplify the measurement, a sample holder was devised in which the water could be measured by a calibrated capillary pipette. A polystyrene plug was inserted in a section of wave guide as shown in Figure 2. A small hole was drilled in the broad side of the guide on level with the top of this plug. A section of copper tubing was soldered over the hole and then connected to a 0.1 ml calibrated pipette by a section of rubber tubing. The other end of the pipette was closed with a short section of rubber tubing clamped at the far end. The sample of water was inserted into the system until it covered the polystyrene window to a depth of approximately two millimeters and filled the tubing and pipette to the top end of the range of the pipette. An adjustable clamp was then used to squeeze the short section of rubber tubing, thereby changing the volume of water in the wave guide by a very small amount as measured by the pipette.

The section of wave guide containing the water sample was installed in a temperature bath which could be maintained at any temperature between 0 and 50 degrees centigrade. Approximately 20 minutes were allowed between temperature changes and measurements to permit the sample to reach an equilibrium temperature.

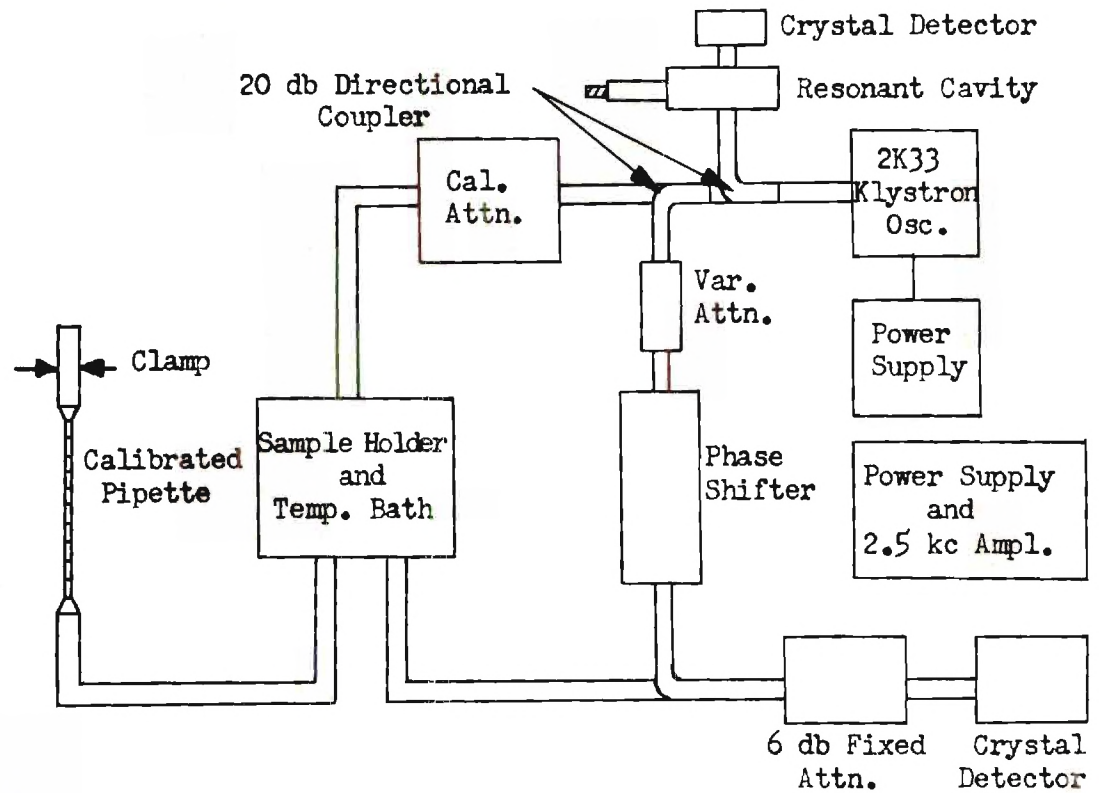


Figure 1.

Simplified Schematic of Laboratory Arrangement for
Measuring Attenuation and Phase Shift through Water Sample

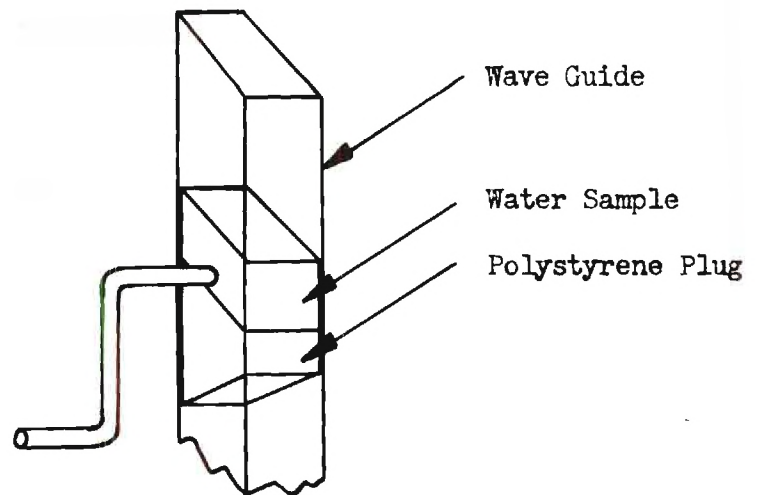


Figure 2.

Water Sample Holder for Transmission Measurements
of Attenuation and Phase Shift in Wave Guide

A directional coupler was inserted immediately in front of the klystron which fed a signal to a transmission type cavity for frequent frequency measurements. Another crystal detector and tuned amplifier were used to detect this signal. The klystron frequency could be measured to plus or minus ten megacycles per second or 0.04 per cent.

For absorption measurements the attenuator in the reference phase arm was completely inserted, thus eliminating all signal to the final crystal except that through the water sample. The calibrated attenuator was adjusted to give a certain meter reading for a given water level in the sample holder. The water path was increased and measured by the pipette; then the attenuator was readjusted to give the same meter reading. The difference between the attenuator settings thus gave the attenuation for a given thickness of water, completely independent of the crystal and amplifier characteristics. The crystal detector was well matched to the line, and the six db fixed attenuation further reduced the standing wave between the crystal and the sample.

For phase measurements a signal was taken from the klystron by a directional coupler, fed through an attenuator and phase shifter, and then back into the line through another directional coupler at a level equal to the level of the signal through the water path. The phase shifter was adjusted to give a minimum meter reading -- i.e., to cancel the signal through the water. Then the water path was increased thus increasing the phase shift through the sample until another minimum meter reading was reached, thereby determining the water path necessary for approximately a 2π phase shift. Since large absorption accompanied this phase shift the new minimum will be somewhat less than 360 degrees as shown in the following derivation.

Referring to equation (3) and holding \underline{t} constant, we let

$$A e^{-\frac{2\pi k}{\lambda_0} \underline{z}} \quad , \quad e^{-j \frac{2\pi n}{\lambda_0} \underline{z}}$$

and

$$B e^{-j\phi}$$

represent the fields at the crystal detector due to the signals through the water and reference arms respectively. \underline{A} and \underline{B} are initially set equal by the attenuators in each arm, and ϕ is adjusted by the phase shifter in the reference arm to give a minimum resultant signal as indicated by the meter. Assuming zero phase at the sample arm, ϕ would be 180 degrees in this case. The resultant power may then be represented by

$$R^2 = A^2 \left[e^{-\frac{4\pi k}{\lambda_0} \underline{z}} - 2e^{-\frac{2\pi k}{\lambda_0} \underline{z}} \cos\left(\frac{2\pi n}{\lambda_0} \underline{z}\right) + 1 \right].$$

Differentiating this with respect to \underline{z} and setting it equal to zero gives a minimum point when

$$\sin\left(\frac{2\pi n}{\lambda_0} \underline{z}\right) = \frac{k}{n} \left[e^{-\frac{2\pi k}{\lambda_0} \underline{z}} - \cos\left(\frac{2\pi n}{\lambda_0} \underline{z}\right) \right]. \quad (8)$$

It is readily seen that only when \underline{k} is zero do successive minima occur at 360 degrees. With the measured value of \underline{z} from the first to the second minimum, and the previously determined value of \underline{k} , this equation

was solved for n by Newton's method. An additional correction due to the decrease in unfilled wave guide by the increase in water height of course had to be made.

There was some doubt as to the mode in which the energy was propagated through the sample and also as to the exact temperature of the water inside of the sample holder; however, an alternate method using two pyramidal horns immersed in water gave essentially the same results. The faces of the horns were covered with a thin sheet of lucite and placed face to face in a water tight container as shown in Figure 3. The transmitting horn was fastened to this container while the receiving horn was free to pivot on an arc of two feet. A micrometer head was used to change the spacing between the two horns. To increase the ease of reading, a dial gauge indicator was used to measure the change in spacings. Some error was introduced by loss at the edges of the horns and by change in parallelism, but this error was considered negligible for the very small changes in horn face spacings inherent in this particular method.

Figure 4 shows a photograph of the complete laboratory arrangement. The water surrounding and between the horns is circulated through copper tubing in a temperature bath shown on the extreme right side of this photograph. The measuring techniques and calculations are the same as given in the preceeding discussion. This method possesses some advantages over the other, especially in the ease with which different water samples such as distilled and salt water could be changed.

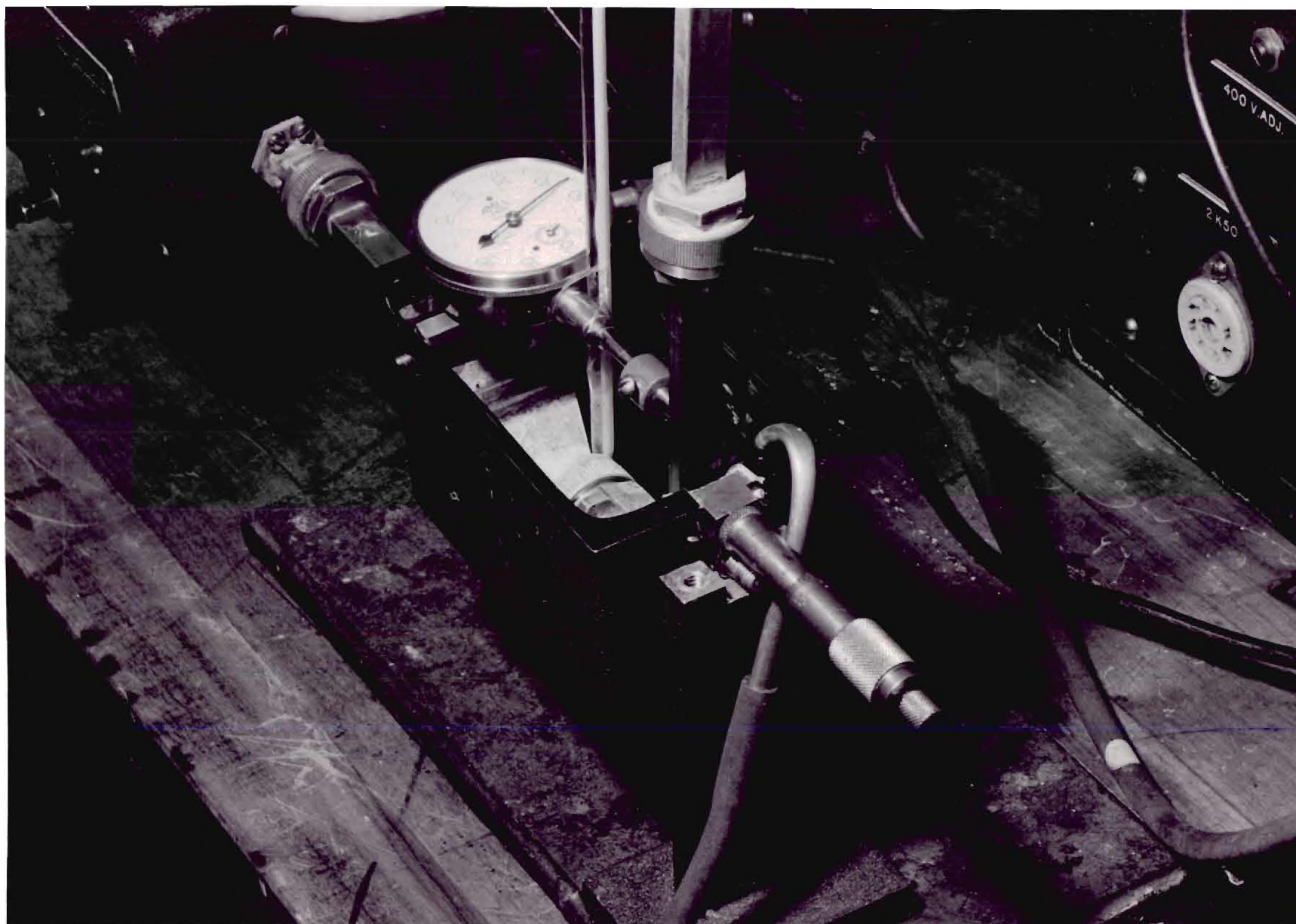


Figure 3.
Sample Holder for Measurement of Attenuation and Phase Shift
of Centimeter Microwaves by Water

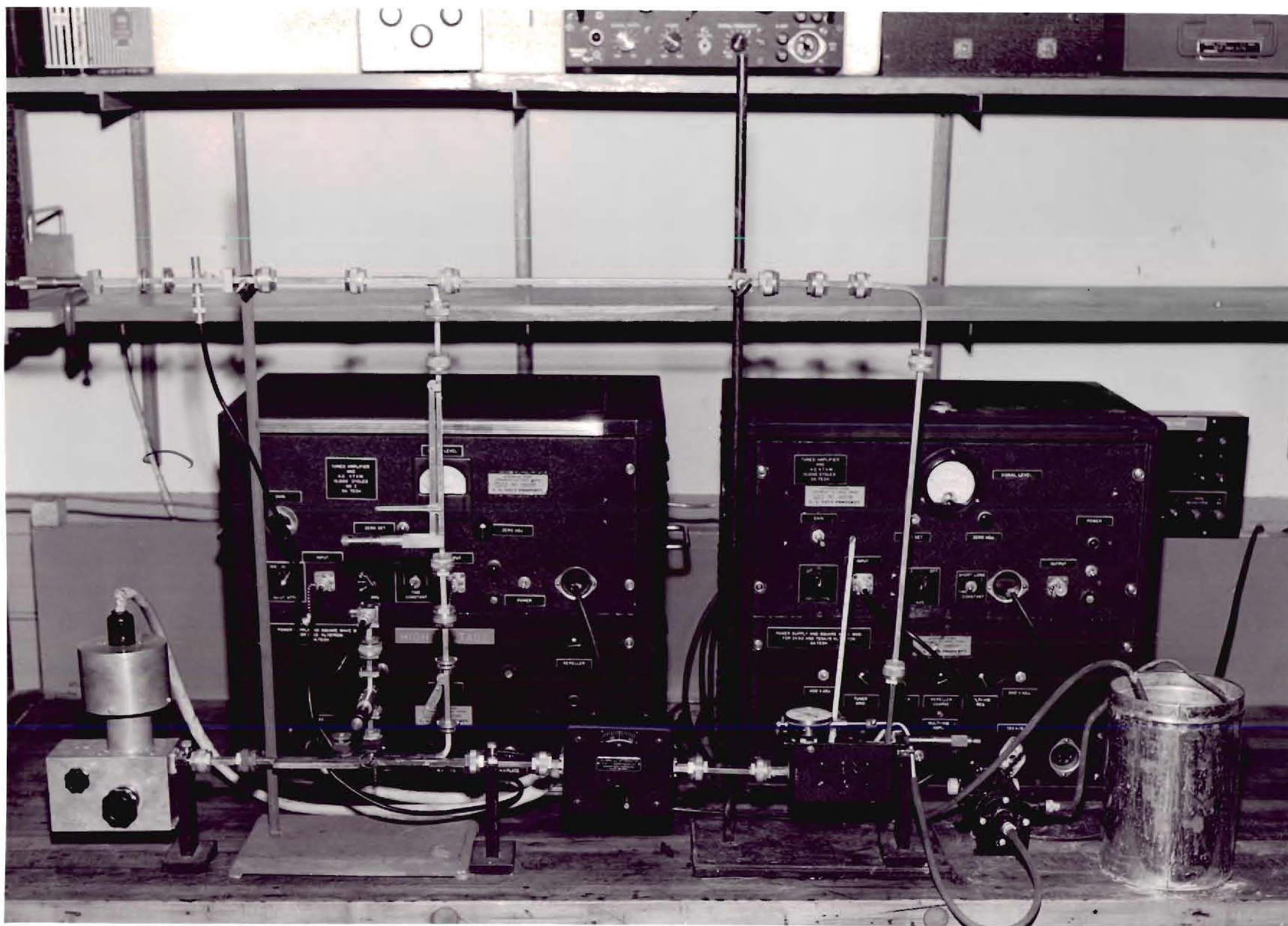


Figure 4.
Laboratory Arrangement for Measurement of Attenuation and Phase Shift
of Centimeter Microwaves by Water

THEORETICAL AND EXPERIMENTAL VALUES

An accepted expression for the relative dielectric constant of a polar liquid or gas in the region of dipolar dispersion is

$$\epsilon = \epsilon' - j\epsilon'' = \epsilon_0 + \frac{\epsilon_s - \epsilon_0}{1 + j\omega\tau}, \quad (9)$$

where ϵ_0 is the dielectric constant at the high frequency end of the dipolar dispersion; ϵ_s is the static dielectric constant; ω is the frequency of the impressed field in radians per second; and τ is the relaxation time of the molecular dipole. The particular theory used or the expression used for the internal field determines the value of the dipole relaxation time. This equation is derived by several methods in the next section using the different internal field expressions of Clausius-Mosotti and Onsager.

If we equate real and imaginary parts of equation (9) we find

$$\epsilon' = \frac{\epsilon_s + \epsilon_0(\omega\tau)^2}{1 + (\omega\tau)^2} \quad (10)$$

and

$$\epsilon'' = \frac{\omega\tau(\epsilon_s - \epsilon_0)}{1 + (\omega\tau)^2}. \quad (11)$$

The variation of ϵ_s with temperature is well known while ϵ_0 is considered to be relatively constant with temperature. Debye has given a value of 2.2 for ϵ_0 for water found in the infra-red region of the spectrum. Saxton⁷ has found that a value more nearly 5.5 fits his experimental results more closely. This is the value one would expect

to measure somewhere between the cm and infra-red regions. The values of ϵ_s , ϵ_o , and T as given by Saxton are reproduced here in Table I.

TABLE I
STATIC AND HIGH FREQUENCY DIELECTRIC CONSTANTS
AND RELAXATION TIME OF WATER AS GIVEN BY SAXTON

Temperature ($^{\circ}\text{C}$)	ϵ_s	ϵ_o	$T \times 10^{-12}$ sec.
0	88	4.5	19.05
5	86	5.0	14.60
10	84	5.5	11.85
15	82	5.5	9.60
20	80	5.4	8.10
25	78.2	5.4	6.80
30	76.4	5.3	5.95
40	73.0	5.2	4.60

The expressions for \underline{n} and \underline{k} in terms of ϵ_s , ϵ_o , ω , and T are found by substituting equations (10) and (11) into equations (6) and (7).

$$2n^2 = \sqrt{\frac{\epsilon_s^2 + \epsilon_o^2(\omega T)^2}{1 + (\omega T)^2}} + \frac{\epsilon_s + \epsilon_o(\omega T)^2}{1 + (\omega T)^2} \quad (12)$$

$$2k^2 = \sqrt{\frac{\epsilon_s^2 + \epsilon_o^2(\omega T)^2}{1 + (\omega T)^2}} - \frac{\epsilon_s + \epsilon_o(\omega T)^2}{1 + (\omega T)^2} \quad (13)$$

The positive value of the radical is taken in both equations to give real values for \underline{n} and \underline{k} .

If the equation for \underline{k} is differentiated with respect to frequency and set equal to zero, the condition for the maximum value of \underline{k} is given as

$$\omega T = \sqrt{\frac{\epsilon_o + 3\epsilon_s}{3\epsilon_o + \epsilon_s}} \quad (14)$$

The values of the relaxation time given in Table I were determined from this equation after Saxton found the frequencies for maximum k at different temperatures. As will be shown below, the experimental results reported here are in excellent agreement with theory* as to the points of maximum k . This indicates that the values of λ given by Saxton are good.

Table II gives the values for n and k computed from the values of Table I using equations (12) and (13). The experimental values obtained by the methods previously described at 1.15, 1.25, and 1.35 cm are also included. A plot of the values of n and k against temperature is shown in Figure 5. The solid line is the calculated curve; the crosses are the experimental values obtained by the writer; the circles indicate the experimental values obtained by Collie, Hasted and Ritson⁸ at 1.27 cm. The latter values are not tabulated.

TABLE II
THEORETICAL AND EXPERIMENTAL VALUES OF n AND k

°C	1.15 cm				1.25 cm				1.35 cm			
	k		n		k		n		k		n	
	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.
0	2.79	2.72	4.83	4.33	2.78	2.80	5.03	4.62	2.80	2.86	5.19	4.74
5	2.83	2.86	5.14	5.02	2.93	2.93	5.34	5.20	2.96	2.95	5.56	5.32
10	2.88	2.90	5.54	5.50	2.88	2.92	5.69	5.71	2.93	2.93	5.84	5.81
15	2.84	2.89	5.78	6.10	2.87	2.88	5.93	6.20	2.85	2.86	6.23	6.30
20	2.77	2.81	6.13	6.35	2.80	2.78	6.41	6.53	2.79	2.73	6.56	6.65
25	2.72	2.68	6.40	6.70	2.58	2.64	6.75	6.90	2.65	2.56	6.85	6.97
30	2.56	2.56	6.64	6.95	2.45	2.48	7.00	7.12	2.52	2.39	7.05	7.21
40	2.35	2.21	7.02	7.30	2.22	2.12	7.39	7.44	2.30	2.00	7.34	7.50
50	2.12		7.32		2.02		7.60		2.04		7.60	

*The words, theory and theoretical, are used loosely here since the parameters, ϵ_s , ϵ_0 , and λ , were found by experiment.

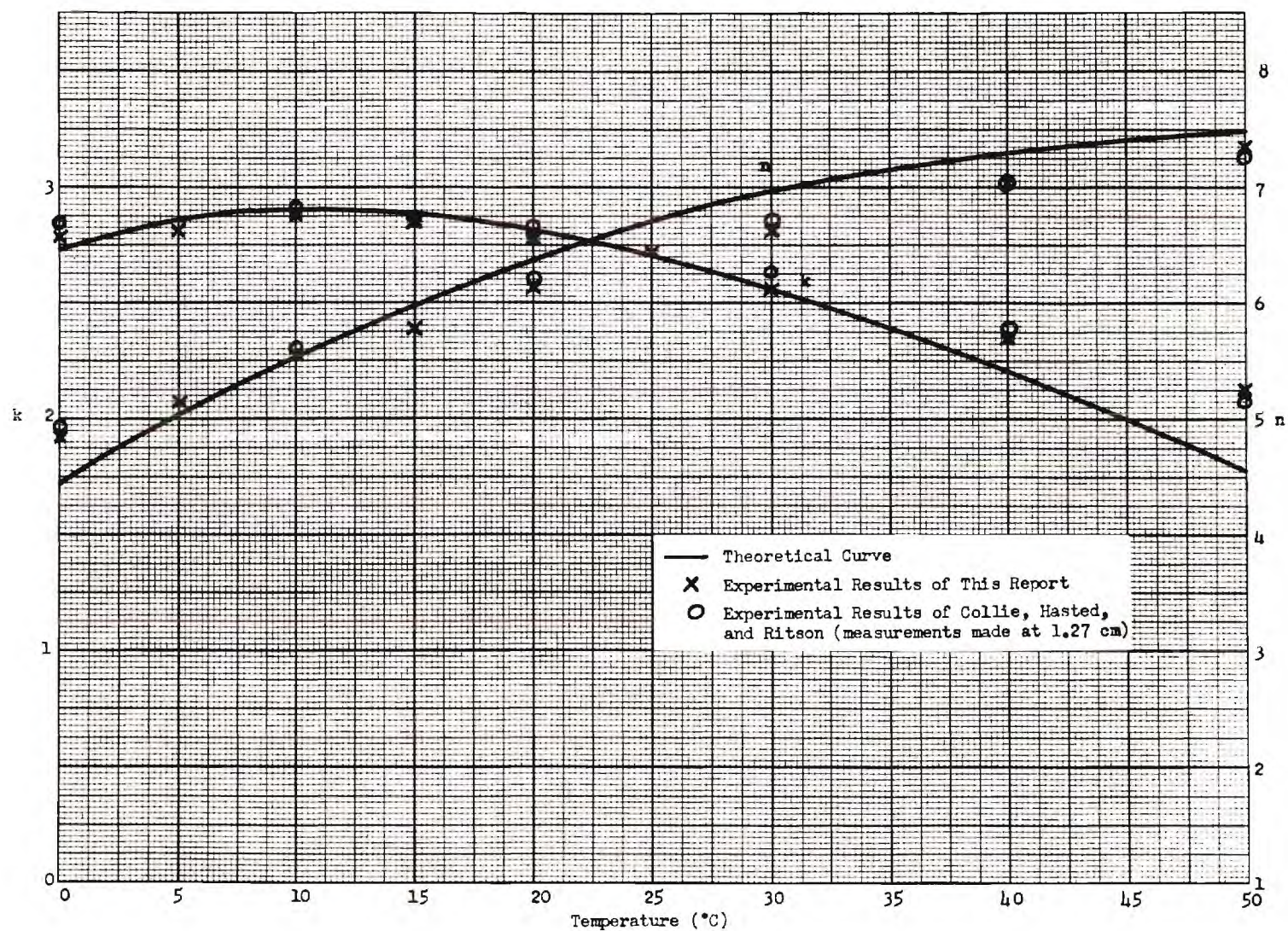
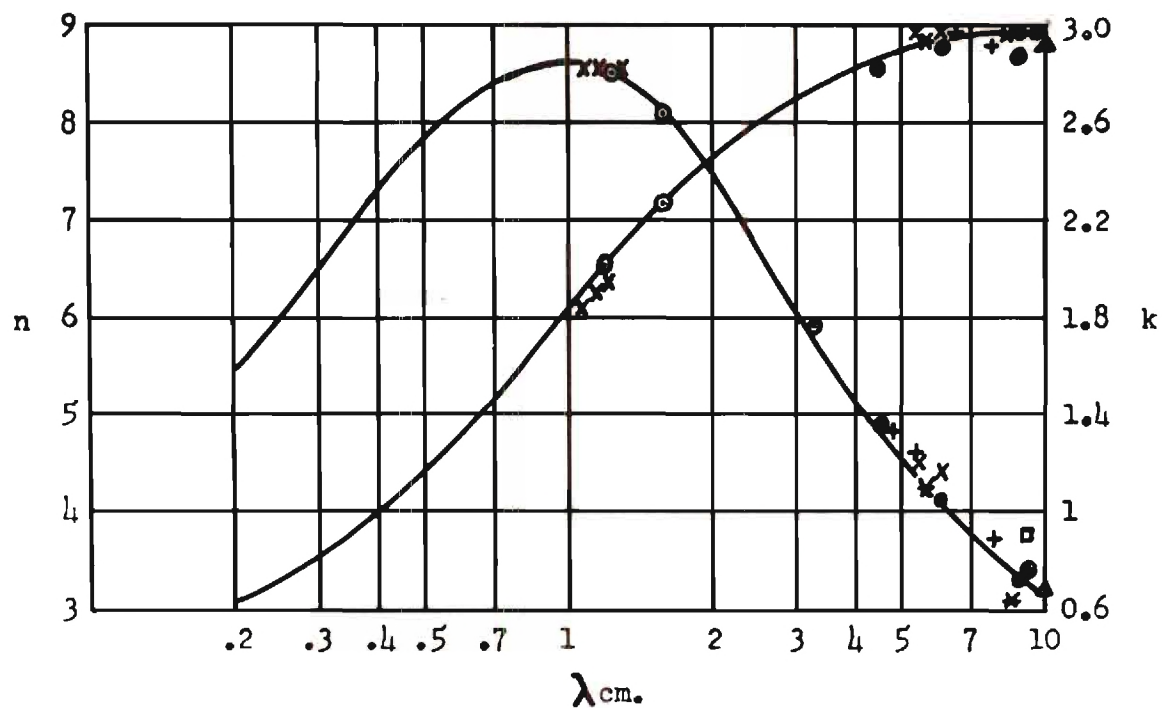


Figure 5.
The Absorption Coefficient and Index of Refraction of Water versus Temperature at 1.25 cm

Figure 6 is a plot of \underline{n} and \underline{k} found from equations (12) and (13) from 0.2 to 10 cm using the values of Table I. Experimental values of various investigators including the values reported in this paper are shown. The experimental values are in good agreement with the values determined by these equations in this region and also for longer wave lengths. It is hoped that future work at shorter wave lengths will verify these equations in this region.



- | | |
|---------------------------|-----------------------|
| ⊙ Saxton and Lane | ● Esau and Baz (1937) |
| ⊕ Manchester University | + Kner (1937) |
| △ Von Hippel | * Eckert (1913) |
| □ Connor and Smyth (1943) | ✕ Author's Results |

Note: This graph is taken from Saxton.⁷

Figure 6.

Theoretical Curves Showing Variation of Absorption Coefficient, k , and Refractive Index, n , with Wave Length (temperature = 20°C)

DISCUSSION OF RESULTS

The experimental results obtained by this work are in good agreement with theory and with the experimental results of others. Measurements at 20 degrees centigrade at 1.25 cm showed no difference between various concentrations of salt water, distilled or tap water. This was not expected since Saxton and Lane⁹ obtained a considerable variation in the absorption coefficient with various concentrations of salt solutions at 1.58 cm.

The attenuator used in the absorption measurements was calibrated at 1.25 cm by the manufacturers. The attenuator was corrected for measurements at 1.15 and 1.35 cm. This correction may be in error since no accurate method was found available for the calibration. It is estimated that the maximum error in k is three per cent. The final values recorded were an average of numerous measurements. The phase measurements are considered to be more accurate since measurements could be repeated to less than one per cent.

The experimental and theoretical values for the dielectric constant of water have not been tabulated in this paper. To find the experimental values at the frequencies at which measurements were made, n and k are substituted into equations (6) and (7). The theoretical values may be found at any wave length between 1.15 centimeters and infinite wave length by equation (9) using the values from Table I. As mentioned previously, future work may prove the validity of equation (9) for wave lengths less than one cm.

DIELECTRIC THEORY IN THE REGIONS OF DIPOLAR DISPERSION

Debye has developed a general expression for the distribution function of molecular moments affected by varying electromagnetic fields using the theory of the Brownian movement. The distribution function is a function of the time, orientation of the molecular dipoles, relaxation time, and temperature. The differential equation containing the distribution function has been derived in the Appendix and is rewritten here.

$$2\lambda \frac{\partial f}{\partial t} = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left[\sin \theta \left(\frac{\partial f}{\partial \theta} - \frac{fM}{KT} \right) \right]. \quad (15)$$

To solve this equation for f we take the real part of the impressed field on a molecule in the liquid which gives us a torque,

$$\tilde{M} = -\mu \tilde{F}_0 e^{j\omega t} \sin \theta.$$

We try as a solution,

$$f = A \left[1 + \frac{B\mu}{KT} \tilde{F}_0 e^{j\omega t} \cos \theta \right].$$

If we drop higher than the first powers of F , equation (15) will be satisfied if

$$B = \frac{1}{1 + j\omega \tau},$$

giving the distribution function as

$$f = A \left[1 + \frac{1}{1 + j\omega \tau} \frac{\mu \tilde{F}_0}{KT} e^{j\omega t} \cos \theta \right]. \quad (16)$$

The mean electric moment of the molecule is found using Boltzmann statistics by

$$\bar{m} = \frac{\int f d\Omega \mu \cos \theta}{\int f d\Omega},$$

which may be evaluated as

$$\bar{m} = \frac{\mu^2 \tilde{F}_0 e^{j\omega t}}{3KT (1 + j\omega \tau)}.$$

The polarization of the liquid due to the permanent dipoles is given by the mean electric moment multiplied by the number of molecules per unit volume or

$$\tilde{P}_\mu = \frac{n\mu^2}{3KT} \frac{\tilde{F}_0 e^{j\omega t}}{1 + j\omega \tau}.$$

If we consider α to be the polarizability of the molecules due to distortion or atomic polarization, the polarization due to distortion may be given as

$$\tilde{P}_\alpha = n\alpha \tilde{F}_1 e^{j\omega t}.$$

It should be noticed that we have not attempted to find an expression for the forces upon the molecules since these forces will drop out of the expressions in later substitutions. The total polarization of the liquid per unit volume is the sum of the polarizations due to orientation and that due to distortion, or

$$\tilde{P} = n \left[\alpha \tilde{F}_1 e^{j\omega t} + \frac{\mu^2}{3KT} \frac{\tilde{F}_0 e^{j\omega t}}{1 + j\omega \tau} \right]. \quad (17)$$

From classical electrostatics the electric displacement, D , in a dielectric medium is defined by

$$\tilde{D} = k_0 \tilde{E} + \tilde{P}, \quad (18)$$

where k_0 is the permittivity of free space; \tilde{E} is the impressed field across the dielectric; and \tilde{P} is the polarization. In numerous simple isotropic dielectric substances, the polarization is approximately proportional to the impressed electric field by a dimensionless constant, χ , called the dielectric susceptibility or

$$\tilde{P} = \chi_e k_0 \tilde{E},$$

giving

$$\tilde{D} = k_0 \tilde{E} + \chi_e k_0 \tilde{E} = k \tilde{E} \quad (19)$$

and

$$k = \epsilon k_0 = (1 + \chi_e) k_0,$$

where k is the permittivity of the medium and ϵ^{**} is the dielectric constant. The substitution for D in equation (18) gives

$$\tilde{P} = k_0 (\epsilon - 1) \tilde{E}. \quad (20)$$

Equating this polarization with that of equation (17), entering n and k_0 into the constant, C , and dropping the periodic variations of the forces, we have

**The dielectric constant is represented by k in many texts, but is left as ϵ in this paper to prevent confusion with the absorption coefficient.

$$C \cdot (\epsilon_s - 1) \tilde{E} = \alpha \tilde{F}_1 + \frac{\mu^2 \tilde{F}_0}{3KT (1 + j\omega \tau)} . \quad (21)$$

If we denote the value of ϵ for high frequencies by ϵ_o and for low frequencies the static value of the dielectric constant ϵ_s and set the frequency first large and then zero we find

$$C \cdot (\epsilon_o - 1) \tilde{E} = \alpha \tilde{F}_1$$

and

$$C \cdot (\epsilon_s - 1) \tilde{E} = \alpha \tilde{F}_1 + \frac{\mu^2 \tilde{F}_0}{3KT} .$$

Substituting these back into equation (21) we have

$$\epsilon = \epsilon_o + \frac{\epsilon_s - \epsilon_o}{1 + j\omega \tau} . \quad (22)$$

Theory of Debye

Instead of using the simple expression for the polarization given by equation (20), Debye used the polarization given from the use of the Clausius-Mosotti internal field.

Clausius and Mosotti considered the actual force acting upon a particle carrying a unit positive charge as consisting of three forces: F_1 , F_2 , and F_3 . The force, F_1 , was due to the actual electric field across the dielectric. The component of force, F_2 , is thought of as an additional force due to the presence of the dielectric excluding a small sphere surrounding the particle assuming the particle to be absent. The component, F_3 , is the force due to the material contained within this small sphere. Due to the complexity of F_3 and since it has

been assumed to be small, it has been neglected. The field inside of a spherical cavity is then given by

$$\tilde{F} = \tilde{E} + \frac{\tilde{P}}{3k_0} . \quad (23)$$

Debye assumed the average moment of one molecule to be

$$\tilde{m} = \alpha \tilde{F} ,$$

where α is the polarizability. If n is the number of molecules, the polarization is given by

$$\tilde{P} = n\tilde{m} = n\alpha\tilde{F} = n\alpha\left(\tilde{E} + \frac{\tilde{P}}{3k_0}\right) .$$

Substituting for \tilde{P} the classical expressions, $\tilde{D} = k\tilde{E} = k_0\tilde{E} + \tilde{P}$, we have

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{n\alpha}{3k_0} . \quad (24)$$

If both sides of this equation are multiplied by the quotient of the molecular weight, M , and the density, ρ , and Avogadro's number, N , is set equal to $\frac{nM}{\rho}$, we obtain

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{N\alpha}{3k_0} = P_{(w)} . \quad (25)$$

Debye defines the right hand side of this equation as the Molar Polarization, $P_{(w)}$, which should more properly be called the Molar Polarizability. In place of our equation (17) Debye has left out the forces, giving for the Molar Polarization,

$$P_{(w)} = \frac{4\pi}{3} N \left[\alpha + \frac{\mu^2}{3KT} \frac{1}{1 + j\omega\tau} \right]. \quad (26)$$

where $\frac{4\pi}{3} N$ is the number of molecules per molar volume. If we equate equations (25) and (26) and define the static and high frequency dielectric constants as we have done previously, we obtain

$$\epsilon = \frac{\frac{\epsilon_s}{\epsilon_s + 2} + j\omega\tau \frac{\epsilon_o}{\epsilon_o + 2}}{\frac{1}{\epsilon_s + 2} + j\omega\tau \frac{1}{\epsilon_o + 2}}. \quad (27)$$

This differs from our expression for the dielectric constant only in the fact that $\omega\tau$ in our expression is replaced by $\frac{\epsilon_s + 2}{\epsilon_o + 2} \omega\tau$ in Debye's expression. The actual values of τ support the first expression for the dielectric constant.

Theory of Onsager

Onsager has derived an alternate expression for the internal field, as he was not satisfied with Debye's use of the Clausius-Mosotti internal field. He represents a polar molecule as a point dipole in the center of a spherical cavity in an isotropic dielectric liquid of dielectric constant, ϵ . The radius, a , of this cavity is of the order of the radius of the molecule.

The internal field acting on the dipole may be represented as the sum of two fields, \tilde{R} and \tilde{G} . The reaction field, \tilde{R} , is caused by the polarization of the surrounding medium by the field of the dipole and acts parallel to the instantaneous direction of the dipole moment. The cavity field, \tilde{G} , is caused by and acts in the same direction as the

applied field, \tilde{E} . In terms of the dielectric constant, dipole moment and radius, these fields may be expressed as

$$\tilde{R} = \frac{2(\epsilon - 1)}{2\epsilon + 1} \frac{\tilde{m}}{a^3} \quad (28)$$

and

$$\tilde{G} = \frac{3\epsilon}{2\epsilon + 1} \tilde{E}. \quad (29)$$

Reference to any standard text (such as Electromagnetism by Slater and Frank) will show these equations derived in detail. The reaction field above is not strictly applicable to any actual liquid since the field is uniform only in an ellipsoidally shaped cavity.

If μ is the permanent dipole moment in free space and u is a unit vector in the direction of μ and α is the distortion polarizability, the dipole moment will be given as

$$\tilde{m} = \mu \tilde{u} + \alpha (\tilde{R} + \tilde{G}) = \mu \tilde{u} + \frac{3\epsilon}{2\epsilon + 1} \alpha \tilde{E} + \frac{2(\epsilon - 1)}{2\epsilon + 1} \frac{\alpha}{a^3} \tilde{m}.$$

Solving this equation for \tilde{m} we have

$$\tilde{m} = \frac{\mu \tilde{u} + \frac{3\epsilon}{2\epsilon + 1} \alpha \tilde{E}}{1 - \frac{2(\epsilon - 1)}{2\epsilon + 1} \frac{\alpha}{a^3}}. \quad (30)$$

The radius of the cavity, a , as defined by Onsager, is given by

$$\frac{4\pi}{3} N a^3 = 1 \text{ cm}^3,$$

and the polarizability α is given in terms of the internal index of refraction by

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N \alpha.$$

By substituting the above expressions for α and \underline{a} in equation (30), the following equation is obtained:

$$\tilde{m} = \frac{(n^2 + 2)(2\epsilon + 1)}{3(2\epsilon + n^2)} \mu \tilde{u} + \frac{\epsilon(n^2 + 2)}{2\epsilon + n^2} \alpha \tilde{E}$$

or

$$\tilde{m} = \mu' \tilde{u} + \beta \tilde{E}.$$

The torque acting on this dipole is

$$\tilde{T} = (\tilde{R} + \tilde{G}) \times \tilde{m}.$$

Since \tilde{R} is parallel to \tilde{m} , $\tilde{R} \times \tilde{m} = 0$ and $\tilde{E} \times \tilde{E} = 0$.

$$\begin{aligned} \tilde{T} &= \tilde{G} \times \tilde{m} = \frac{3\epsilon}{2\epsilon + 1} \tilde{E} \times (\mu' \tilde{u} + \beta \tilde{E}) \\ &= \frac{3\epsilon}{2\epsilon + 1} \mu' \tilde{E} \times \tilde{u} = \frac{\epsilon(n^2 + 2)}{2\epsilon + n^2} \mu \tilde{E} \sin \theta = \mu^* E \sin \theta. \end{aligned}$$

The potential energy is then equal to

$$U = -\mu^* E \cos \theta.$$

The component of \tilde{m} in the direction of \tilde{E} is

$$\tilde{m}_E = \mu' \cos \theta + \beta \tilde{E}.$$

In order to find \overline{m}_E (the average value of \tilde{m}_E) it is necessary to find the average value of $\cos \theta$. Using Boltzmann statistics we obtain

$$\overline{\cos \theta} = \frac{\int_0^{2\pi} \int_0^{\pi} e^{-\frac{U}{KT}} \cos \theta \sin \theta \, d\theta \, d\phi}{\int_0^{2\pi} \int_0^{\pi} e^{-\frac{U}{KT}} \sin \theta \, d\theta \, d\phi}.$$

For fields sufficiently small that powers of $\frac{\mu^* E}{3KT}$ higher than the first are negligible, the above expression becomes

$$\overline{\cos \theta} = \frac{\mu^* E}{3KT},$$

giving for \bar{m}_E

$$\begin{aligned} \bar{m}_E &= \frac{\mu^* \mu}{3KT} \tilde{E} + \beta \tilde{E} \\ &= \left[\frac{(n^2 + 2)^2 (2\epsilon + 1) \mu^2}{3(2\epsilon + n^2)^2 3KT} + \frac{\epsilon(n^2 + 2)}{2\epsilon + n^2} \alpha \right] E. \end{aligned} \quad (31)$$

α and \bar{m}_E may be eliminated by substituting

$$\alpha = \frac{3}{4\pi N} \frac{n^2 - 1}{n^2 + 2}$$

and

$$\bar{m}_E = \frac{\tilde{P}}{N} = \frac{\epsilon - 1}{4\pi N} \tilde{E}.$$

After simplification

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)^2} = \frac{4\pi N \mu^2}{9KT}. \quad (32)$$

If we substitute for \underline{n} the high frequency dielectric constant ϵ_0 and

consider $2\epsilon \gg \epsilon_o$ we obtain

$$2(\epsilon - \epsilon_o) = \frac{4\pi N\mu^2}{9KT} (\epsilon_o + 2)^2,$$

which is the usual expression for Onsager's equation for the dielectric constant of a polar liquid. If we consider ϵ_o as fairly independent of temperature we may write this as

$$(\epsilon - \epsilon_o) = \frac{A\mu^2}{KT}.$$

Also we may enter the relaxation time as Debye did giving

$$\epsilon = \epsilon_o + \frac{A\mu_o^2}{KT(1 + j\omega\tau)}.$$

Solving for A by setting ω first equal to zero and then infinity, we obtain for ϵ ,

$$\epsilon = \epsilon_o + \frac{\epsilon_s - \epsilon_o}{1 + j\omega\tau}. \quad (33)$$

This is the same equation we derived previously and have used on page 14.

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REFERENCES

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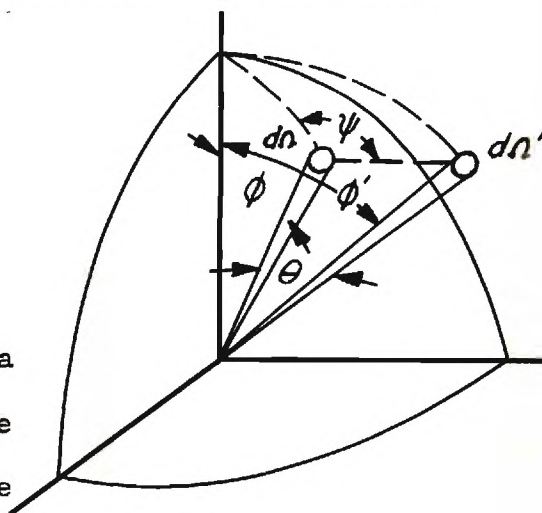
APPENDIX

APPENDIX

THE DISTRIBUTION FUNCTION FOR MOLECULAR DIPOLES

We consider an impressed field constant in direction but varying sinusoidally with time across a small spherical region in a dielectric medium. We take the center of the sphere in this liquid as the center of our polar coordinate system. The number of molecules which at a given time have their moments in the direction of a solid angle $d\Omega$ is $f d\Omega$. The varying field and the Brownian movement vary this number.

Now suppose that at an interval of time, δt , later all of these molecular moments have shifted outside of the solid angle $d\Omega$ but the element of time, δt , is still small enough that these moments have not shifted more than a few degrees. During this interval of time the number of molecules whose moments have entered $d\Omega$ is given by



$$\delta t \frac{\partial f}{\partial t} d\Omega = \Delta_1 + \Delta_2, \quad (A1)$$

where the contribution, Δ_1 and Δ_2 , are due to the rotations produced by the impressed field and Brownian movement, respectively.

In order to discuss the contributions by the Brownian movement Δ_2 , we imagine a second solid angle, $d\Omega'$, at an angle, Θ , with the axis of $d\Omega$. We assume a certain probability function, W , such that $W d\Omega$ denotes the probability that a molecule whose moment lies in $d\Omega'$

at $t = 0$ will have its moment in $d\Omega$ at $t = \delta t$. Integrating over the sphere and holding $d\Omega$ constant, the total of the molecular moments entering $d\Omega$ is then

$$\Delta_2 = -f d\Omega + \int f' d\Omega' W d\Omega, \quad (A2)$$

where f' is the distribution function corresponding to the angle ϕ' . The first term, $f d\Omega$, accounts for all moments that pass out of $d\Omega$ which were originally there, and the second term accounts for all moments originally outside $d\Omega$ which are now within the solid angle. It is clear that the probability function, W , will be a function of θ alone, while the space variation of f will depend on ϕ alone. We may write

$$\Delta_2 = d\Omega \left[\int f' W d\Omega' - f \right]. \quad (A3)$$

If we expand f' about its value at $d\Omega$ we obtain

$$f' = f + (\phi' - \phi) \frac{\partial f}{\partial \phi} + \frac{(\theta' - \theta)^2}{2} \frac{\partial^2 f}{\partial \theta^2} + \dots$$

According to the second restriction on δt , W must approach zero very rapidly when θ exceeds a few degrees. In order to evaluate the integral above we need therefore consider only small values of θ or therefore $(\phi' - \phi)$. Letting $(\phi' - \phi) = y$ gives

$$\int f' W d\Omega' = f \int W d\Omega' + \frac{\partial f}{\partial \phi} \int y W d\Omega' + \frac{1}{2} \frac{\partial^2 f}{\partial \theta^2} \int y^2 W d\Omega' + \dots$$

The first integral on the right equals unity; the second represents the

mean value \bar{y} of y ; and the third, the mean square value of y^2 of y .

These may be evaluated giving

$$\bar{y} = \frac{\bar{\theta}^2 \cos \phi}{4 \sin \phi}, \quad (\text{A4})$$

where

$$\bar{\theta}^2 = \int_0^\pi \int_0^{2\pi} \theta^2 W \sin \theta \, d\theta \, d\phi$$

and

$$\bar{y}^2 = \frac{\bar{\theta}^2}{2}, \quad (\text{A5})$$

which gives

$$\int f W \, d\Omega = f + \frac{\partial f}{\partial \phi} \frac{\cos \phi}{\sin \phi} \frac{\bar{\theta}^2}{4} + \frac{\bar{\theta}^2}{4} \frac{\partial^2 f}{\partial \theta^2}. \quad (\text{A6})$$

Substituting equation (A6) into equation (A3) we have

$$\Delta_2 = d\Omega \frac{\bar{\theta}^2}{4} \left[\frac{\cos \phi}{\sin \phi} \frac{\partial f}{\partial \phi} + \frac{\partial^2 f}{\partial \theta^2} \right]. \quad (\text{A7})$$

It can be seen that if the molecular moments have a random distribution (i.e., if f is independent of ϕ) the Brownian movement can have no effect on the distribution function. In the case of an impressed electric field the distribution function will not be uniform, and hence will be affected by the Brownian movement.

In order to find Δ_1 , the number of molecular moments entering $d\Omega$ during δt , we consider the torque on the molecule tending to orient it in the direction of the field,

$$\tilde{M} = -\mu \tilde{F} \sin \phi .$$

With a constant torque the molecule would be accelerated until it reached its so-called terminal velocity where the frictional torque, proportional to the velocity, would balance the impressed torque, or

$$\tilde{M} = \xi \frac{d\phi}{dt} .$$

If we consider the acceleration time negligibly small, the molecule will turn through an angle,

$$\int \phi = \int t \frac{\tilde{M}}{\xi} ,$$

in the time interval, $\int t$. Now if we draw a circle around this sphere at an angle, ϕ , from the axis, the number of molecular moments that pass through this circle will be

$$2\pi f \sin \phi \int \phi = 2\pi f \frac{\tilde{M}}{\xi} \int t \sin \phi . \quad (A8)$$

The number of moments that pass through another circle, $\phi + d\phi$, in the same interval of time is

$$2\pi f \frac{\tilde{M}}{\xi} \int t \sin \phi + \frac{\partial}{\partial \phi} (2\pi f \frac{\tilde{M}}{\xi} \int t \sin \phi) d\phi . \quad (A9)$$

Δ_1 will then be the difference between these or

$$\Delta_1 = - \frac{\partial}{\partial \phi} (2\pi f \frac{\tilde{M}}{\xi} \int t \sin \phi) d\phi . \quad (A10)$$

By substituting equations (A7) and (A10) into equation (A1) and

remembering that $d\Omega = 2\pi \sin \vartheta d\vartheta$, we have

$$\frac{\partial f}{\partial t} = \frac{1}{\sin \vartheta} \left[\sin \vartheta \left\{ \frac{\bar{\theta}^2}{4\delta t} \frac{\partial f}{\partial \vartheta} - \frac{\tilde{M}}{\xi} f \right\} \right]. \quad (A11)$$

For the special case when the impressed field is constant or $\frac{\partial f}{\partial t} = 0$, the Maxwell Boltzmann expression must satisfy this equation,

$$\frac{\bar{\theta}^2}{4\delta t} \frac{\partial f}{\partial \vartheta} - \frac{\tilde{M}}{\xi} f = 0. \quad (A12)$$

From the Maxwell Boltzmann expression, $f = A e^{-\frac{U}{KT}} = A e^{-\frac{\mu \tilde{F} \cos \vartheta}{KT}}$,

$$\frac{\partial f}{\partial \vartheta} = A \frac{\mu \tilde{F} \sin \vartheta}{KT} e^{-\frac{\mu \tilde{F} \cos \vartheta}{KT}}.$$

Therefore,

$$\frac{\bar{\theta}^2}{4\delta t} = \frac{KT}{\xi}. \quad (A13)$$

The distribution function may then be found from this differential equation:

$$\xi \frac{\partial f}{\partial t} = \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left[\sin \vartheta (KT \frac{\partial f}{\partial \vartheta} - \tilde{M} f) \right]. \quad (A14)$$

To find the relaxation time, the time for the moments to revert to a random distribution after the removal of the impressed field, we set $\tilde{M} = 0$ and solve the above equation.

$$\xi \frac{\partial f}{\partial t} = \frac{KT}{\sin \vartheta} \frac{\partial}{\partial \vartheta} (\sin \vartheta \frac{\partial f}{\partial \vartheta}). \quad (A15)$$

We try as a solution,

$$f = A \left[1 + \frac{\mu_{F_0}}{KT} \psi(t) \cos \phi \right], \quad (A16)$$

where ψ is yet to be found. The equation is satisfied if

$$\psi = e^{-\frac{2KT}{\xi} t}.$$

Thus

$$f = A \left[1 + \frac{\mu_{F_0}}{KT} e^{-\frac{2KT}{\xi} t} \cos \phi \right]. \quad (A17)$$

The variable part of the distribution function will be reduced to $\frac{1}{e}$ of its initial value after a time of $\frac{\xi}{2KT}$ seconds. The relaxation time is then defined as

$$\tau = \frac{\xi}{2KT}. \quad (A18)$$

Substituting this into equation (A14), we have the differential equation for the distribution function:

$$2\tau \frac{\partial f}{\partial t} = \frac{1}{\sin \phi} \frac{\partial}{\partial \phi} \left[\sin \phi \left(\frac{\partial f}{\partial \phi} - \frac{fM}{KT} \right) \right]. \quad (A19)$$

This is identical to equation (15) on page 21.